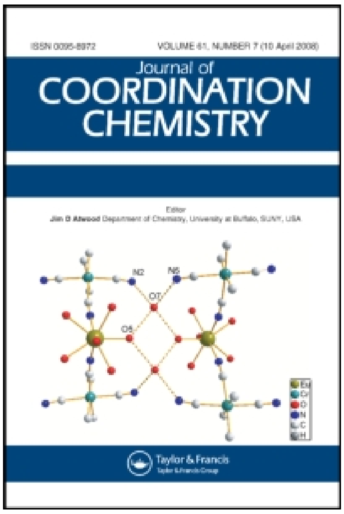

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Kantekin, Halit and Gök, YaşLar(1999) 'THE SYNTHESIS AND CHARACTERIZATION OF A NEW TETRAOXIME AND ITS DINUCLEAR COMPLEXES', Journal of Coordination Chemistry, 46: 3, 283 — 290
To link to this Article: DOI: 10.1080/00958979908048473
URL: http://dx.doi.org/10.1080/00958979908048473

J. Coord. Chem., 1999, Vol. 46, pp. 283–290
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THE SYNTHESIS AND CHARACTERIZATION OF A NEW TETRAOXIME AND ITS DINUCLEAR COMPLEXES

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(Received 17 October 1997)

A novel *bis*(dioxime) (**H_4L**) containing the hexaoxa macrocyclic moiety has been synthesized from the reaction of tetraaminodibenzo-18-crown-6 (**1**) and 2,3-butanedione monooxime (**2**). An octahedral cobalt(III) complex of this ligand was prepared by the oxidation of the cobalt(II) complex. The BF_2 bridged cobalt(III) complex was achieved by using the hydrogen bridged cobalt(III) complex and boron trifluoride. The structures of the *bis*(dioxime) and its complexes are proposed according to elemental analysis, ^1H and ^{13}C NMR, IR and MS data.

Keywords: *bis*(dioxime); cobalt(III); BF_2^+-capped complex; template effect; crown ether; macrocycle

INTRODUCTION

Many questions concerning the dependence of the biofunctionally important reactivities of the B_{12} coenzymes on their structural characteristics are still open to discussion.[1] Coenzyme B_{12} is known to act as a cofactor in a series of complex enzymatic reactions.[2] Model studies in search of the mechanism for the enzymatic reactions catalysed by coenzyme B_{12} and methyl cobalamin, the only known organocobalt compounds in nature, exceeded this objective and have become a general contribution to inorganic and coordination chemistry.[3] This aspect has been brought together in a highly creative and productive way as commented upon by Halpern.[4] The biochemical reactivity of cobalamin coenzymes is largely influenced by axial ligation through electronic effects. The influence of electronic effects

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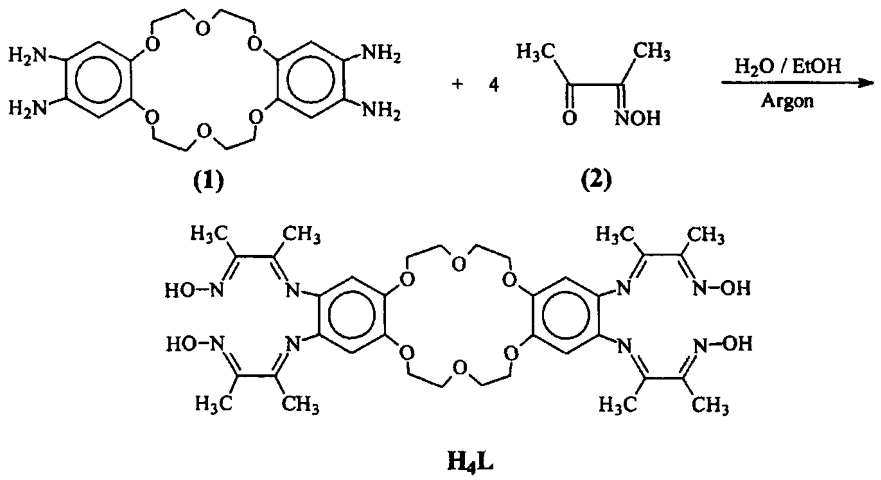
on the Co–N bond lengths, concerning axial ligation, in non-organometallic Costa-type complexes were studied by Gerli and Marzilli and their co-workers;[5] this reveals lengthening of the Co–N distance with the σ-donor capability of the *trans* axial ligands.

Crown ethers first synthesized by Pedersen,[6] have been the focus of much interest for the past thirty years because of the chemical and biological applications of their ion-binding, solvation and transport effects.[7] Recently, crown ethers have also been employed to construct new compounds with extraordinary properties, such as ion channels,[8] catalysts[9] and recognition aspects.[10] Macrocyclic polyethers contain central hydrophilic cavities with either electronegative or electropositive binding atoms and flexible exterior frameworks exhibiting hydrophobic character.[11]

The hard ether-containing macrocycles show a binding preference towards hard alkaline or alkaline earth cations, but incorporation of soft azomethine units causes a preference towards soft heavy metal cations.[12] The present compound has features of both transition metal chemistry and crown-ether chemistry in the same molecule.

RESULTS AND DISCUSSION

To synthesize the macrocyclic moiety (Scheme 1) in the **H_4L** ligand, four molecules of 2,3-butanedione monoxime (**2**) were coupled *via* a tetraamine



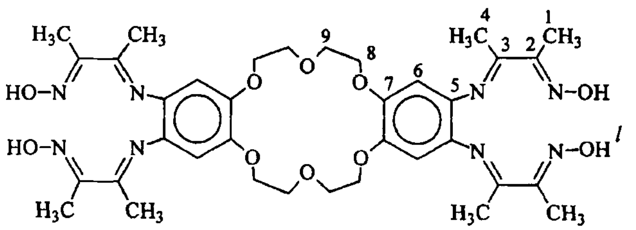
SCHEME 1

group by reaction with tetraamino(dibenzo-18-crown-6)[13] (**1**) in H_2O/EtOH mixture. The resulting product **H_4L** was obtained in *ca* 42% yield after recrystallization from a mixture of water and ethanol. The structure of the ligand and its complexes was determined by a combination of elemental analysis, ^1H and ^{13}C NMR, IR and MS data.

The proton magnetic resonance spectrum of the ligand gives a sharp singlet at $\delta = 11.45$ ppm corresponding to four hydroxyimino groups. This resonance is also easily identified by D_2O exchange. The chemical shifts for N–OH protons indicate that the oxime groups are in the (E, E) form. The other chemical shifts belonging to aromatic and methyl protons, which are equivalent two by two, appear as sharp singlets at $\delta = 7.32$, 2.45 and 2.05 ppm, respectively. They are very similar to those of the precursor amine and monoxime compounds. In the ^{13}C NMR spectrum of the ligand, the carbon resonances of the oxime groups are found at lower fields ($\delta = 154.88$ and 152.20 ppm). The equivalent carbon resonances of the proton-decoupled ^{13}C spectrum of oxime groups confirm the (E, E) form of the *bis*(dioxime) (Table I). On the other hand, the inequivalent carbon resonances at $\delta = 32.42$ and 24.00 ppm can be attributed to methyl groups. The IR spectrum of **H_4L** shows no characteristic absorption assignable to either C=O or NH_2 belonging to the precursor compounds and (**1** and **2**). Sharp bands of medium intensity at 1593 and 1582 are attributed to C=N groups.[14] A similar band at 1208 cm^{-1} is assigned to N–O stretching.[3,15] Fast atom bombardment of this ligand showed an expected molecular ion peak at $m/z = 753$ $[M + 1]^+$.

Complexation of the ligand with cobalt(II) chloride was intended to obtain a hexacoordinated cobalt(III) complex when oxygen was bubbled

TABLE I ^{13}C NMR data for H_4L



H_4L

Position	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_{8-9}
δ (ppm)	32.42	154.88	152.20	24.01	144.11	108.55	139.05	70.49–69.68

through a suspension of $[Co_2(H_2L)]$. As a consequence, four axial ligands had to be selected in addition to the equatorial deprotonated ligand. Depending on the charge carried by the axial ligands, neutral, cationic or anionic complexes can be obtained. Since the equatorial ligands contribute a single negative charge, two neutral axial ligands are required to obtain an anionic cobalt(III) complex. This complex obtained has a metal : ligand ratio of 2 : 1 according to the result of the elemental analysis data. The FAB (positive) mass spectrum of $[Co_2Na(H_2L)L'Cl_2](ClO_4)_3$ exhibited intense peaks at $m/z = 1415$ and 1315 corresponding to $[M+1]^+$ and $[M\text{-}ClO_4]^+$.

In the ^1H NMR spectrum of cobalt(III) complex, the presence of protons involved in intramolecular hydrogen bonds at around $\delta = 17.42$ ppm are identified. In the IR spectrum, the characteristic bands of the free ligand are shifted and lowered in intensity on complex formation, and new resonances for the complex appear.[14,16] The broad band at 3153 cm^{-1} in the free ligand is shifted to 2414 cm^{-1} in the cobalt(III) complex; this can be attributed to the intramolecular hydrogen bond.[3,17] The complex exhibits sharp strong bands at 1580 and 1571 cm^{-1} assignable to C=N vibrations of coordinated azomethine groups. An unique feature is the occurrence of new bands at 787 and 536 cm^{-1}. In agreement with detailed IR studies on cobaloxime,[15] the former is assigned to C–H deformation vibrations of coordinated pyridine and the latter to Co–N stretching. Perchlorate anions exhibit strong absorptions at around 1100 and 620 cm^{-1}; the absence of splitting of these bands (ν_3 and ν_4) indicates that the perchlorate anions are uncoordinated.[18]

In this study, the synthesis of a BF_2 derivative of the hydrogen bonded cobalt(III) complex was accomplished by heating and stirring a heterogeneous mixture of $[Co_2Na(H_2L)L'_2Cl_2](ClO_4)_3$ in dry acetonitrile with boron trifluoride etherate. The latter reagent readily reacted with the O–H O bridge in the molecule *via* the template effect, affording an extremely stable compound containing O–BF_2–O bridges.[14] The broad band at 2414 cm^{-1} in the precursor cobalt(III) compound disappears in the BF_2 derivative. On the other hand, this complex resembles that of hydrogen bonded analogues except for B–O and B–F bands and the absence of ν' (N–O) bands. The sharp band at 1188 and 841 cm^{-1} and a weak band at 1050 and 1017 cm^{-1} in BF_2^+-capped cobalt(III) complex are ascribed to stretching of B–O and B–F, respectively.[19] The vibrations at 1580 and 1571 cm^{-1} belonging to C=N groups in the precursor cobalt(III) complex are shifted to 1600 and 1588 cm^{-1} with higher intensity in the BF_2-bridged complex. This indicates the stability and strength of the coordinate bond due to the strong electron-withdrawing influence of the BF_2 groups incorporated in the macrocycle.[20] In the proton NMR spectrum of this complex, the disappearance of O–H O signal is noted. The other proton resonances appear downfield relative to the precursor. Fast atom bombardment mass spectra exhibit a molecular ion peak at $m/z = 1509$ due to $[M+1]^+$.

EXPERIMENTAL

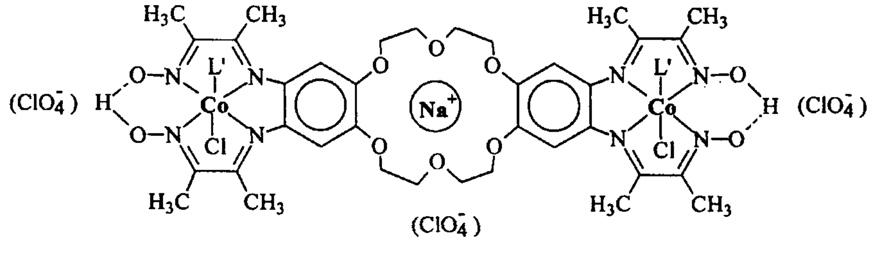
^1H and ^{13}C NMR spectra were recorded on either a Varian 300-XL or a Varian Gemini 200 spectrometer. Chemical shifts (δ) are reported in ppm relative to teramethylsilane using the solvent signal as internal reference. Fourier transform infrared spectroscopy using KBr pellets was performed on a Perkin-Elmer 1600 FT-IR instrument. Fast atom bombardment (FAB) mass spectra were recorded on a VG AutoSpec from VG Analytical (*m*-nitrobenzylalcohol as matrix). Elemental analyses and metal contents of the complexes were determined by a Hewlett-Packard 185 CHN analyser and Unicam 929 AA spectrophotometer. Melting points were measured on an Electrothermal apparatus and are uncorrected. Tetraaminodibenzo (18-crown-6) was prepared by a reported procedure.[13] Cobalt(II) chloride hexahydrate (Merck) and 2,3-butanedione monoxime (Fluka) were used as received for the synthesis of ligand and complexes. Boron trifluoride ethyl ether complex (Fluka) was distilled just before use. Commercially available pure grade solvents, dried and purified by conventional procedure,[21] were used.

3,3′,8,8′-Tetramethyl-5,5′,6,6′-dibenzo(18-crown-6)-4,4′,7,7′-tetra-azadideca-3,3′,7,7′-tetraene-2,2′,9,9′-tetraone tetraoxime, H_4L

A stirred solution of 2,3-butanedione monoxime (1.60 g, 15.9 mmol) (**2**) in water (160 cm^3) at 35°C and under an atmosphere of argon, was added dropwise over 2 h to a solution of tetraaminodibenzo(18-crown-6) (**1**) (1.65 g, 3.97 mmol) in ethanol (400 cm^3) at 45°C. The reaction mixture was stirred and refluxed for 35 h under inert conditions. The end of the reaction was determined by thin layer chromatography [$R_f = 0.47$, $CHCl_3$: MeOH : H_2O (73 : 25 : 2)]. After cooling to room temperature, the reaction mixture was concentrated to 50 cm^3 under reduced pressure, and the mixture was cooled in a refrigerator at −5°C overnight, whereupon the product precipitated from the reaction mixture. The dark yellow precipitate was filtered off, washed with water and cold ethanol and then dried *in vacuo*. After crystallization from ethanol : water (3 : 2), the yield was 1.25 g (42.23%) of yellow product, m.p. 257°C. ^{1}H NMR (DMSO-d_6): δ 11.45 (s, 4H, OH), 7.32 (s, 4H, Ar-H), 4.20–3.15 (m, 16H, CH_2OCH_2), 2.45 (s, 6H, CH_3), 2.05 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6): δ 154.88, 152.20, 144.11, 139.05, 108.55, 70.49–69.68, 32.42, 24.00. IR (KBr pellets, cm^{-1}): 3135 (O–H), 3045 (Ar–H), 2922 (C–H), 1593 (C=N), 1582 (C=N), 1208 (N–O). Mass spectrum (FAB positive): $m/z = 753\ [M+1]^+$. Found: C, 57.63; H, 6.15; N, 15.05. Calc. for $C_{36}H_{48}N_8O_{10}$: C, 57.44; H, 6.38; N, 14.89%.

Synthesis of $[Co_2Na(H_2L)L'_2Cl_2](ClO_4)_3$ (L' = pyridine), 3

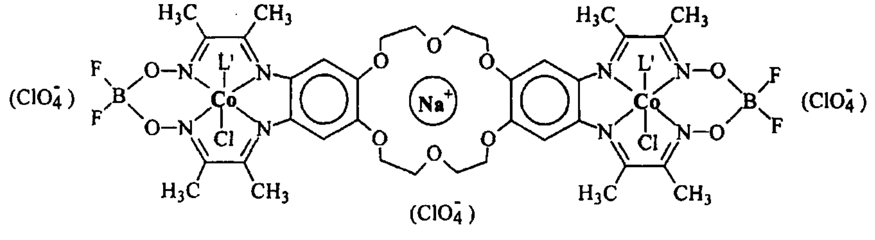
A solution of $CoCl_2 \cdot 6H_2O$ (0.51 g, 2.13 mmol) in ethanol (25 cm^3) was added to a hot solution of ligand (**H_4L**) (0.80 g, 1.06 mmol) in ethanol (80 cm^3) with stirring at 60°C. A solution of pyridine (0.18 g, 2.13 mmol) in ethanol (3 cm^3) and a saturated solution of $NaClO_4$ (5.2 cm^3) were added to the mixture. The reaction mixture was allowed to cool to room temperature, and a stream of oxygen was bubbled through the solution for 3 h. The solution was concentrated under reduced pressure to 20 cm^3, whereupon the solid product crystallized. The dark brown product was filtered off, washed with cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.50 g (33.11%), m.p. 307–309°C. ^{1}H NMR (DMSO-d_6): δ 17.42 (s, 2H, O–H O), 8.27 (m, 4H, py-H), 7.78–7.40 (m, 6H, Ar-H, py-H), 7.28 (m, 4H, py-H) 4.34–3.22 (m, 16H, CH_2OCH_2), 2.51 (s, 6H, CH_3), 2.12 (s, 6H, CH_3). IR (KBr pellet, cm^{-1}): 3029 (Ar–H), 2950 (C–H), 2414 (O–H O), 1580 (C=N), 1571 (C=N), 1197 (N–O). Mass spectrum (FAB positive): $m/z = 1415\ [M+1]^+$, $1315\ [M\text{-}ClO_4]^+$, $1216\ [M\text{-}2ClO_4]^+$. Found: C, 39.08; H, 3.78; N, 9.60; Co, 8.12. Calc. for $C_{46}H_{56}N_{10}O_{22}Cl_5Co_2Na$: C, 38.91; H, 3.94; N, 9.87; Co, 8.31%.



(3)

Synthesis of $[Co_2Na(LB_2F_4)L'_2Cl_2](ClO_4)_3$ (L' = pyridine), 4

The hydrogen-bonds in the *pseudo* octahedral cobalt(III) complex $[Co_2Na(H_2L)L'_2Cl_2](ClO_4)_3$ were replaced by BF_2 by reaction of the complex with boron trifluoride ethyl ether complex by following reported procedures.[12] A suspension of $[CO_2Na(H_2L)L'_2Cl_2](ClO_4)_3$ (0.423 g, 0.3 mmol) in 75 cm^3 of freshly distilled dry acetonitrile was brought to 45°C in an argon atmosphere. A large excess of boron trifluoride ethyl ether complex (0.20 cm^3) was added with continuous stirring to the suspension, which changed colour to reddish brown. The reaction mixture was allowed to stand at the same temperature for 5 h and the end of the reaction was verified by using TLC [$R_f = 0.51$, *n*-BuOH : AcOH : H_2O(4 : 1 : 5)]. The solvent was removed under reduced pressure and the residue dissolved in 20 cm^3 of dry acetonitrile, then the last step was repeated twice. The red solution was cooled to −15°C overnight and the product was filtered off, washed with cold acetonitrile and diethyl ether and then dried *in vacuo*. Yield: 0.31 g (68.8%); m.p. 282°C. ^1H NMR (DMSO-d_6): δ 8.18 (m, 4H, py-H), 7.70–7.33 (m, 6H, Ar-H, py-H), 7.11 (m, 4H, py-H), 4.30–3.28 (m, 16H, CH_2OCH_2), 2.42 (s, 6H, CH_3), 2.06 (s, 6H, CH_3). IR (KBr pellets, cm^{-1}): 3040 (Ar–H), 2958 (C–H), 1600 (C=N), 1588 (C=N), 1208 (N–O). Mass spectrum (FAB positive): $m/z = 1509$ $[M+1]^+$. Found: C, 36.30; H, 3.56; N, 9.24; Co, 7.78. Calc. for $C_{46}H_{54}N_{10}O_{22}NaCl_5B_2F_4\ Co_2$: C, 36.46; H, 3.56; N, 9.24; Co, 7.78%.



(4)

Acknowledgements

The authors thank the Research Fund of Karadeniz Technical University (Trabzon, Turkey) for financial support and Professor D.H. Busch (University of Kansas) for assistance with NMR and MS data.

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